SYNTHESIS OF LIGHT OLEFINS FROM
SYNGAS VIA DIMETHYLETHER
— A NEW TECHNIQUE PROCESS

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Abstract　　A new route named as SDTO method for the synthesis of light olefins from syngas has been proposed. That is to convert syngas to dimethylether and then to convert dimethylether to light olefins. The catalysts for the two conversion reactions have been developed. For the first reaction, the catalyst was synthesized by the combination of methanol synthesis catalyst with γ-Al_2O_3 or zeolites which possesses both metallic and acidic functions. The catalyst for the second reaction was modified SAPO-34 molecular sieve. The variables of the reactions have also been investigated. The results from the serial connection of the two conversion steps without any separation show that the yield of $C_2^=$ — $C_4^=$ olefins could be > 100 g/ (m^3 syngas).

Keywords　light olefin, syngas, dimethylether, SAPO-34

Introduction

The synthesis of lower olefins from coal or natural gas via syngas is one of the most important non-oil routes for ethylene and propylene production. Two methods were suggested for light olefins synthesis from syngas, one is the direct method by which syngas is directly converted to light olefins[1], the other is the indirect method via methanol or the MTO method[2] which is to convert syngas to methanol and then to convert methanol to light olefins. Many significant results have been obtained

since 1970's[3-8]. In accordance with the facts that the direct method is thermodynamically unfavorable and the products may be restricted by the Schulz-Flory rule, and the methanol has to be converted to dimethylether prior to light olefins during indirect conversion process. We propose a new route named as SDTO method which is to convert syngas to dimethylether and then to convert dimethylether to light olefins. The new route has apparent advantages in enhancing CO conversion and simplifying the process.

Experimental

The catalyst for conversion of syngas to dimethylether was prepared by the combination of methanol synthesis catalyst (Cu-Zn-Al) with γ-Al$_2$O$_3$ or zeolites. The catalysts were tabulated and crushed to 15—35 mesh for reaction. The reaction was carried out on a $\Phi 8 \times 300$ mm stainless steel, fixed-bed, continuous flow reactor. On-line thermal conductivity detector (TCD) chromatograph with Porapak-Qs and carbon molecular sieve type 601 (Shanghai) columns was used to analyze the reaction products.

Silicoaluminophosphate SAPO-34 and modified SAPO-34 were used as the catalyst for the conversion of dimethylether to lower olefins. The catalytic reaction was carried out either on a $\Phi 12 \times 285$ mm quartz fixed bed reactor or on a $\Phi 20 \times 500$ mm fluid bed reactor under normal pressure. Products were analyzed on line by using Porapak-Qs column and TCD detector.

Results and discussion

1. *Conversion of syngas to dimethylether*

The syngas conversion in methanol synthesis reaction on conventional metal catalysts is not very high because the reaction is restricted thermodynamically. When the catalyst possesses both metal and acid properties, there exist three main paths in the reaction:

$$CO + 2H_2 \longrightarrow CH_3OH \tag{1}$$

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \tag{2}$$

$$H_2O + CO \longrightarrow H_2 + CO_2 \tag{3}$$

The methanol formed in reaction (1) can convert to dimethylether immediately through dehydration reaction (2) on acid sites. Therefore, higher conversion of syngas could be obtained.

Table 1   Reaction results of the bifunctional catalysts[a]

Acidic component	Temp. (°C)	CO conv. (mol. %)	DME/(DME+MeOH) (mol. %)	CH₄ (mol. %)
γ-Al$_2$O$_3$	260	85. 27	91. 59	2. 89
M-γ-Al$_2$O$_3$	260	87. 94	93. 50	2. 24
HY Zeolite	265	81. 65	91. 63	3. 12
M-HY[b]	265	69. 30	92. 12	1. 89
SAPO-5	265	58. 81	59. 17	1. 76
HMd Zeolite	260	92. 28	94. 00	5. 24
M-HMd[b]	260	92. 17	94. 96	2. 12
HZSM-5	240	90. 33	91. 40	3. 09
M-ZSM-5[b]	238	92. 37	92. 57	1. 43

a   metal : acid = 2 : 1 (weight); P = 3. 0 MPa; GHSV = 1000 h⁻¹; H$_2$: CO = 2 : 1
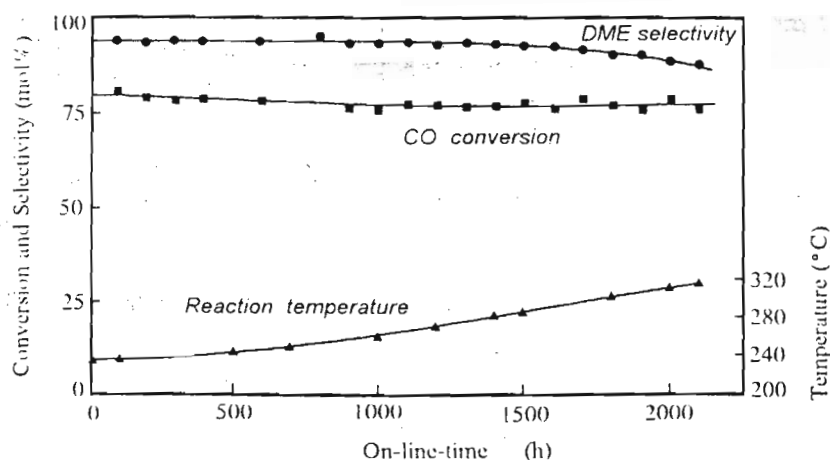b   modified HY, HMd or ZSM-5

Fig. 1   Long-term test of the catalyst for the conversion of syngas to dimethylether (GHSV = 1000 h⁻¹, P = 3. 5MPa)

The reaction results over the metal-acid bifunctional catalysts, which were made from Cu-Zn-Al methanol synthesis catalyst incorporated with various

dehydration components, are listed in Table 1. The dehydration ability of the acidic composition was found having effects on catalytic behavior of the syngas conversion reaction. The catalysts made up of γ-Al_2O_3, modified HMd or modified ZSM-5 zeolite exhibit higher CO conversion and DME selectivity.

The process variables of the reaction have been investigated on M-ZSM-5 or M-HMd modified catalysts. The results show that the suitable reaction conditions may be: $210-280\,^{\circ}C$; $P>3.0$ MPa and GHSV<1500 h^{-1}.

Long-term test of the catalyst has been carried out under the reaction conditions of GHSV $= 1000$ h^{-1} and $P = 3.5$ MPa (Fig. 1). Temperature is raised non-periodically to maintain the CO conversion higher than 75%. Although some accidents happened during the test, for example, the over rising of reaction temperature for many times, the selectivity of dimethylether maintained 90% in the range of $0-2000$ hours and the selectivity to the by-product CH_4 was less than 3%.

2. Conversion of DME or McOH to light olefins

The conversion of DME or other oxygenated compounds, such as methanol, to light olefins is the key step of the SDTO method. Much work has been done on this subject. Pentasil-type zeolites and some narrow pore zeolites such as chabazite and ZSM-34 have been found effective for this purpose[9−12]. Recently, silicoaluminophosphate SAPO-34 and modified SAPO − 34 were found to exhibit good catalytic performance for methanol conversion to light olefins[6,8,13]. In this work, molecular sieve SAPO-34 and modified SAPO-34 samples synthesized by using cheap templeting agent were used as the catalysts for the conversion. Because the pure dimethylether is difficult to obtain in laboratory, methanol was used as reactant in this study.

The modification effects on SAPO-34 by divalent metal ions are shown in Table 2. The addition of the metal ions may result in the decrease of the acidity of the catalyst and the increase of ethylene selectivity. The modified catalyst with medium acidity (SP05-58) exhibits good light olefin selectivity.

The effects of water dilution in the feed were also investigated. The results of methanol conversion over SAPO-34 catalyst are listed in Table 3. As reported in literature[14−16], the increased concentration of water due to dilution may result in the increase of light olefin selectivity and the reduction of the rate of coke formation. The adsorbed water molecules can promote the desorption of the initial formed olefin and then inhibit the formation of the larger molecules, which may be the reason of the water effect.

The results of stream testing in fixed bed reactor show that the activity of the SAPO-34 catalyst decreases within about 2 hours under the reaction conditions of 450°C, WHSV (MeOH) = 2.0 h^{-1}. However the activity could be completely restored by heating the catalyst in a stream of air at 500-650°C. Coking is the main reason of the deactivation. Fluid bed reactor was accounted to be suitable for this type of catalyst.

Table 2   The reaction results of methanol conversion over modified SAPO-34 catalysts[a]

Catalyst	SAPO-34	SPNi04	SPBa05	SPCa01	SPMg03	SPO5-58
			methanol conversion (wt%)			
	100	100	79.99	100	100	100
			Hydrocarbon (wt. %)			
CH_4	8.19	3.81	2.87	2.42	2.68	1.70
C_2H_4	38.66	45.74	51.15	49.03	40.05	57.57
C_2H_6	1.18	1.16	1.50	1.37	2.18	0.76
C_3H_6	33.70	35.00	32.68	34.15	36.11	37.14
C_3H_8	4.52	3.36	2.60	3.66	6.56	1.91
C_4H_8	12.15	9.07	6.12	7.38	9.78	0.93
C_4H_{10}	1.46	2.27	3.08	2.12	2.65	0
C_5^+	0	0	0	0	0	0
$C_2^= - C_3^=$	72.36	80.74	83.83	83.18	76.16	94.71
$C_2^= - C_4^=$	84.51	85.68	89.95	90.56	85.94	95.64

a   fixed bed, reaction temperature: 450°C, WHSV(MeOH) = 2.0 h^{-1}

Table 3   The effect of water dilution on the conversion of methanol[a]

Feed	MeOH	50%MeOH+50%H_2O[b]	30%MeOH+70%H_2O[b]
		Methanol conversion (wt. %)	
	100	99.68	97.88
		Olefin selectivity (wt. %)	
C_2H_4	42.00	52.69	56.10
C_3H_6	35.53	39.00	33.21
C_4H_8	9.40	3.15	6.09
$C_2^= - C_3^=$	77.53	91.69	89.31
$C_2^= - C_4^=$	86.93	94.84	95.40

a   450°C; WHSV(MeOH) = 2.0 h^{-1}; reaction time = 60 min

b   by weight

Table 4 Reaction results in fluid bed reactor[a]

Times of regeneration	0	10	30	60	80	100	
Reaction temp. (℃)	500	530	530	530	530	530	450[b]
	Olefin selec. (%)						
$C_2^=$	35.66	49.49	52.55	52.53	52.33	50.69	42.82
$C_3^=$	39.76	34.09	34.41	31.46	32.08	35.88	40.10
$C_2^= - C_4^=$	87.16	92.19	94.81	92.51	92.66	93.46	86.75

a WHSV$(Me_2O) = 2.0 \ h^{-1}$, Me_2O conversion $= 100\%$
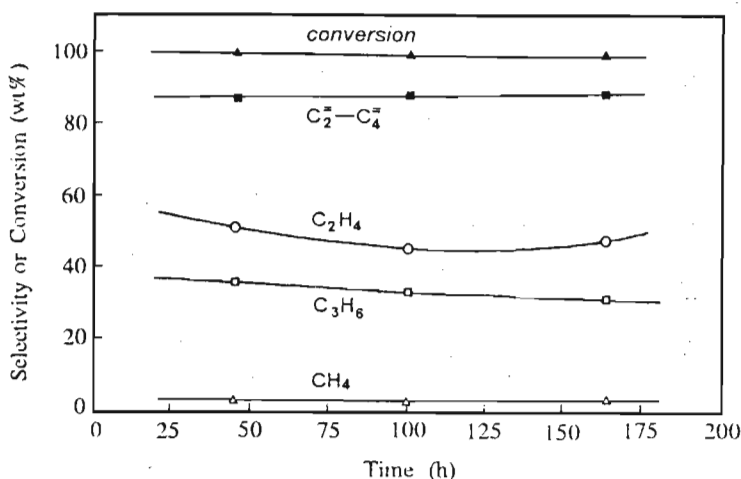
b on fixed bed reactor

Fig. 2 Variation of conversion and selectivity with
calcination time at 800℃ (fixed bed reactor, 450℃,
WHSV (MeOH)$=1.0 \ h^{-1}$, reaction time$= 60$ min.)

The regeneration test of the modified SAPO-34 catalyst was carried out in the
fluid bed reactor. The temperature of decoking reaction in air flow is in the range of
550-650℃. If the temperature is 550℃, the regeneration is finished in 30 minutes,
while the temperature is kept above 600℃, the coke can be removed within 10
minutes. The effects of the times of regeneration on catalytic behavior are listed in
Table 4. After regeneration for about 10 times, the selectivity to light olefins tends
to steady. In the steady state of the catalytic performance, the selectivity to ethylene
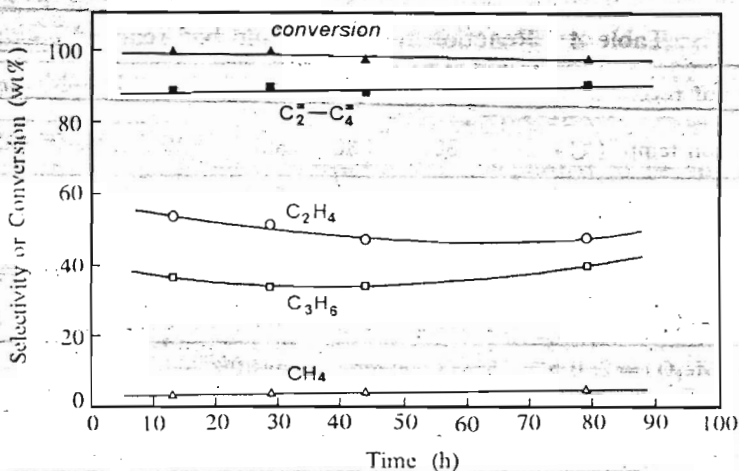$>50\%$, $C_2^= - C_3^= > 80\%$ and $C_2^= - C_4^= > 90\%$.

Fig. 3 Variation of conversion and selectivity with the
time of steam treatment at $800\,°C$
(reaction condition same as in Fig. 2)

Because a large amount of water exists in the products and the catalyst has to be regenerated frequently at high temperature, high stability of the catalyst is needed. Severe conditions were selected under which the stability of the catalyst has been tested. The results are shown in Figs. 2 and 3. The activity and selectivity of the catalyst are almost the same as the fresh catalyst after long time treatment in steam or in air flow at $800\,°C$. The X-ray diffraction results show that only little decrease of the crystallinity of the samples comparing with that of the fresh catalyst. It could be concluded that the developed SAPO-34 molecular sieve catalyst possesses not only high light olefin selectivity but high stability as well.

3. Serial connection of the two conversion steps

The products of the conversion of syngas were used as the reactant of the second reaction without any separation. The results of the connected reactions are listed in Table 5. The selectivity to the light olefins of the second reaction is lower than that of methanol conversion reaction. However, the yield of $C_2^= - C_4^=$ olefins could be about 100 g/m^3 syngas. The deficiency of water in the reaction system and the existence of CO_2 may be the main reasons of the decrease of light olefin selectivity. When diluted with water, the yield of light olefins can be enhanced.

Table 5 Results of the two connected reactions

	The first reaction[a]	The second reaction
Catalyst	Cu-Zn-Al + M-HMd	Modified SAPO-34
React. temp. (°C)	265	450
GHSV (h^{-1})	1000	2000
Pressure (MPa)	4.0	normal pressure
CO conv. (%)	90.35	
DME + MeOH selectivity	99.26	
DME + MeOH conv. (%)	100[b]	100[c]
Light olefins (wt. %)		
$C_2^=$	40.19	56.68
$C_3^=$	34.14	26.84
$C_4^=$	8.03	4.82
$C_2^= - C_4^=$	82.36	88.34
Yield of $C_2^= - C_4^=$ [d]	103	110

a $H_2 : CO = 2 : 1$

b   no water dilution in feed

c   diluted with water, $WHSV(H_2O) = 1.67 \ h^{-1}$

d g/M^3 syngas, calculated results

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